PHASE EQUILIBRIA & DIAGRAMS

→ many identical "things" join together creating PHASES!
PHASE = A CHEMICALLY & STRUCTURALLY HOMOGENEOUS REGION OF THE MATERIAL

→ if I choose T, P, or composition, it can happen THAT THE PHASE OF A SYSTEM CHANGES!
⇒ I NEED TO PLOT A "PHASE DIAGRAM" TO DESCRIBE SUCH BEHAVIOR

→ we draw PHASE DIAGRAMS AT EQUILIBRIUM, therefore WE DO NOT REPRESENT SUPERHEATED SOLIDS & SUPERCOOLED LIQUIDS!

→ COMPONENTS OF A PHASE
"The chemically distinct & essentially indivisible solids"

EXAMPLE: take pure Al

pure Al = show FCC structure
⇒ 1 COMPONENT (Al) @ 1 PHASE (FCC)

• take FCC, add water (liquid)

⇒ 1 component (H₂O) & 2 PHASES (solid ice) + (liquid water)

• take Copper (is FCC, too) Ni, is FCC
Cu + Ni mixed together FORM a random solution of Cu & Ni = SOLID SOLUTION
2 components (Cu) + (Ni) & 1 PHASE (solid solution random FCC)

• Window's glass
SiO₂ + Na₂O + CaO → 3 components (SiO₂) + (Na₂O) + (CaO)
& 1 PHASE (amorphous)!
ONE COMPONENT SYSTEM

WHAT can I change? P, T, Comp (N0) => P&T only
How many degrees of freedom? 2 =>

PHASE DIAGRAM

P - ISOBARS (V & T ISOCORES)

T - ISOThERMS

ONE COMPONENT PHASE DIAGRAM

PRESSURE (atm)

Solid m.p. Liquid gaseous

PRESSURE (atm)

Solid Liquid Vapor

TRIPLE POINT
Solid & Liquid & VAPOUR CONEIST

CRITICAL POINT
Liquid & Vapor become a single DIG FLUID

WATER

ICE III

ICE I

A

B

C

Vapor

Temperature (°C)

Temperature (°C)

Solid

Liquid

220 ATM

1 ATM

SOLID LIQUID

SOLID

Pophile
**GIBBS PHASE RULE**

At equilibrium:
- The number of degrees of freedom (things that we can change) is related to:
  - \( F = C - P + 2 \)
    - \( C \) = number of components
    - \( P \) = number of coexisting phases
    - \( 2 \) = number of state variables

\( \text{If } P \text{ is fixed } \Rightarrow \) 
\( F = C - P + 1 \)

Example: \( \text{H}_2\text{O} \) with water liquid and ice

- \( C = 1 \)
- \( P = 2 \)

\( F = 1 - 2 + 2 = 1 \) ⇒ to have 2 phases, I can change only one variable \( T \) or \( P \). If I change \( P \), \( T \) will follow \( T(P) \). If I change \( T \), \( P \) will follow \( P(T) \).

⇒ Coexistence of 2 phases, with 1 component leads to a curve 1D DIMENSIONLESS **LOCUS**

PE3
2nd Example: Pick H₂O when ice, liquid, vapour coexist \( \Rightarrow C = 1 \) \( P = 3 \)
\[ F = 1 - 3 + 2 = 0 \]
\[ \Rightarrow \text{triple point is a 0-dimensional locus} \]
\[ OD = \text{no freedom} = \text{invariant} \]
\[ \Rightarrow \text{a point} \]

3rd Example: Pick H₂O vapour \( \Rightarrow C = 2 \) \( P = 2 \)
\[ F = 1 - 1 + 2 = 2 \]
\[ \Rightarrow \text{vapour is a 2-dimensional locus, a part of a plane with 2 coordinates to be described} \]
\[ \Rightarrow \text{a region} \]

\[ \begin{array}{c}
\text{P} \\
\end{array} \]

\[ \begin{array}{cccc}
2D & 1D & 2D \\
\end{array} \]

\[ \begin{array}{c}
\text{D} \\
\end{array} \]

\[ \begin{array}{cccc}
4D & 0D & 2D \\
\end{array} \]

\[ \begin{array}{c}
\text{T} \\
\end{array} \]

\[ \text{DIMENSION OF THE LOCUS} \]
MORE COMPLEX ONE COMPONENT SYSTEMS

Iron

Temperature (°C)

Pressure (GPa)

SiO₂

PE5
**Two-Component Systems**

A change in one can change another variable. Concentration of A or B in a mix of A and B.

**Concentrations**

**Weight** or **Atomic**

\[ C_A^\text{w} = \frac{C_A^\text{w}}{W_A} \]

\[ C_A^\text{w} + C_B^\text{w} = 1 \]

**Example**

\[ C_H^\text{w} (\text{H}_2\text{O}) = \frac{2}{2+16} = \frac{1}{9} \]

\[ C_H^\text{w} (\text{H}_2\text{O}) = \frac{2}{2+16} = \frac{1}{9} \]

\[ W_A^\text{a} \& W_B^\text{a} \text{ atomic weight of A and B} \]

\[ C_A^\text{a} \& C_B^\text{a} \text{ atomic concentrations} \]

\[ C_A^\text{w} \& C_B^\text{w} \text{ weight concentrations} \]

**Atomic** ⇒ **Weight**

\[ C_A^\text{w} = \frac{C_A^\text{a} \times W_A^\text{a}}{C_A^\text{a} \times W_A^\text{a} + C_B^\text{a} \times W_B^\text{a}} \]

\[ C_A^\text{w} + C_B^\text{w} = 1 \]

**Molar** mix \( N_A \) moles of A & \( N_B \) moles of B

\[ N_A = \frac{n_A}{n_A + n_B} \]

\[ N_B = \frac{n_B}{n_A + n_B} \]

\[ N_A + N_B = 1 \]

**Solubility**

Put sugar in water = solute & solvent

If \( C_{\text{sugar}} \leq C_{\text{sugar max}} \Rightarrow \text{sugar does not precipitate} \)

\( C_{\text{sugar max}} = \text{solubility line} \)

\( \text{max solute without precipitation} \)

PE6
**ISOMORPHOUS DIAGRAM FOR IDEAL 2-COMPONENTS SYSTEM A&B**

**SIMPLEST CASE**

**DEFINITIONS**

**ISOMORPHOUS** = if you mix A & B, at low temperature they form a **SOLID-SOLUTION**

**WHEN SOLID-SOLUTIONS?** when A & B similar!

**HUME-ROTHERY RULES:**

1. **SIZE A & B OFF OF NA+ 15%**
2. **ELECTRONEGATIVITIES ARE ähnlicher**
3. **VACENCES ARE SIMILAR**
4. **CRYSTAL STRUCTURE OF PURE A & B IS IDENTICAL**

**Ex:** Cu + Ni form a **SOLID-SOLUTION**

Cu ≈ Ni: they are **ISOMORPHOUS**

**DRÁW** COMPOSITION **DIAGRAM**

**CONSTANT** Pressure (1 atm)

**T**

**PURE A**

A

CB

B

T

Tm(A) < Tm(B)

**IDEAL LENS SYSTEM**
FIGURE 7.3-1
The idealized binary (A-B) isomorphous system: (a) the composition-temperature phase diagram with associated definitions, and (b) a similar diagram showing the liquidus and solidus temperatures for a specific alloy of composition \( x_b \).

\[
\text{IDEAL SYSTEM =꺝� SOLID SOLUTION + LENS}
\]

\[
\text{WHY? ORIGIN IS GIBBS RULE CONSISTENCE}
\]

\[
P = \text{const} \implies F = c - P + 1
\]

\[
\text{Look for two phase regions}
\]

\[
\text{Pure A (or B)}
\]

\[
L \quad c = 1 \quad F = 1 - 2 + 1 = 0
\]

\[
\Rightarrow \text{Point @ Coexisting has no freedom}
\]

\[
\text{Mix A+B} \implies c = 2
\]

\[
F = 2 - 2 + 1 = 1 \quad \Rightarrow
\]

\[
\text{There is an interval (A) for which 2 phases coexist!}
\]

\[
\text{PE8}
\]
MEASUREMENT SCHEME

Pure A \( T_m(A) = 1000 \, \text{K} \)

Mix A & B \( C_B = 10\% \Rightarrow \) 2 PHASE INTERVAL \( [900, 700] \, \text{K} \)

\( C_B = 30\% \Rightarrow \) 2 PHASE INTERVAL \( [800, 600] \, \text{K} \)

\( C_B = 60\% \) 2 PHASE INTERVAL \( [700, 500] \, \text{K} \)

Pure B \( C_B = 100 \Rightarrow T_m = 600 \, \text{K} \)

PEG
How much liquid & solid and now which composition they have?

Remember that you are at equilibrium (go up down in temperature very slowly)

Inside a 2-Phases region which concentrations?

Pick concentration & temperature of your mix

\[(C, T) = \text{State point}\]

**FIGURE 7.3-2** Graphical definitions of the tie line and the lever rule in a two-phase field: (a) the tie line through the state point defined by temperature \(T_1\) and alloy composition \(X_b\), and (b) the same tie line shared by all five alloy compositions at temperature \(T_1\).

Draw horizontal line at \((T_1, C)\) there is **tie line**

C or + (back uses + so I use +) but you should try to use c
LEVER RULE

\[ X = \text{conc of B} \]

\[ X_0 \rightarrow \text{How } M_0 \text{ moves} \rightarrow M_L \text{ is liquid} \text{ at conc } X_L \]
\[ M_S \text{ is solid} \text{ at conc } X_S \]

**Conservation of Mass**

\[ M_0 X_0 = M_L X_L + M_S X_S \]

\[ \Rightarrow X_0 = \left( \frac{M_S}{M_0} \right) X_S + \left( \frac{M_L}{M_0} \right) X_L \]

\[ X_0 = f_S X_S + f_L X_L \]

**Conservation of Total Mass**

\[ M_0 = M_L + M_S \Rightarrow 1 = f_L + f_S \]

\[ \begin{aligned}
  f_L + f_S &= 1 \\
  f_S X_S + f_L X_L &= X_0
  \end{aligned} \]

\[ f_S = \frac{X_0 - X_L}{X_S - X_L} = \frac{X_L - X_S}{X_L - X_S} \]

\[ f_L = \frac{X_0 - X_S}{X_L - X_S} = \frac{X_S - X_0}{X_S - X_L} \]

**Solutions**

**But difficult**

**Remember**

**Try Rule**
FIGURE 7.3-3
A schematic illustration of the lever rule. The tie line represents a "lever" with its pivot point located at the alloy composition \( X_0 \), its left end fixed at "position" \( X_L \), and its right end located at \( X_S \) with blocks of mass \( M_L \) and \( M_S \) resting on either end.

\[ M_S \text{ at the RIGHT depends on the LEFT part of the pivot} \]
\[ f_S = \frac{X_0 - X_L}{X_S - X_L} \]

\[ M_L \text{ at the LEFT depends on the LEFT part of the pivot} \]
\[ f_L = \frac{X_S - X_0}{X_S - X_L} \]

\[ \Rightarrow \text{ LIQUID} \]

---

PE12
**EXAMPLE**

Alloy 1
$X_B = 0.21$

$\frac{f_S}{f_L} = \frac{0.21 - 0.2}{0.4} = 0.025$
$NORM = 0.6 - 0.2 = 0.4$
$f_L = 0.975$
Almost All Liquid

Alloy 2
$X_B = 0.3$

$f_S = \frac{0.3 - 0.2}{0.4} = 0.25\%$
$f_L = 75\%$
Most Liquid

Alloy 3
$X_B = 0.4$

$f_L = \frac{0.4 - 0.2}{0.4} = 50\%$
$f_S = 50\%$

Alloy 4
$X_B = 0.5$

$f_L = \frac{0.5 - 0.2}{0.4} = 60\%$
$f_S = 40\%$

Alloy 5
$X_B = 0.59$

$f_L = \frac{0.59 - 0.2}{0.4} = 92.5\%$
$f_S = 2.5\%$
Almost All Liquid

PE13


**Figure 7.3-4** Equilibrium solidification of alloy 1 (composition 0.6 B): (a) the cooling path and sketches showing the development of the microstructure, and (b) an expanded section of part (a) showing the compositions of the liquidus and solidus boundaries in the range of 1010°C to 1060°C.
**Solidification**

![Diagram of solidification process]

**Determination:** Mix, $T \uparrow$, $T \downarrow$ & watch liquid, solid

**Or:** $T \downarrow$ and watch for heat flow out

**Isomorphous systems:** Form solid solution @ low temp

- **Cu-Ni:** FCC
- **NiO-MgO** [Both Ni & Cl] = FCC with bond one amino acid & one cotton

**Why I have lens?** Because of entropy

- A-A bond $E_{AA}$
- B-B bond $E_{BB}$
- A-B bond $E_{AB} = \frac{1}{2}(E_{AA} + E_{BB})$ ideal

$\Rightarrow$ Min energy

**PE15**
But remember that we have to minimize \( G = E + PV-TS \) for entropy effect.

\( T_A \) \( T_B \) \( T_{BM} \) (B)

\( T_A(\beta) \) \( T_B(\beta) \) MIN ENERGY \( C_B(\beta) \)

\( @ \) const P, \( \beta \) T

\( C_B(\beta) \) in ideal straight line \( \Rightarrow \)

\( X_B \) & \( X_A = 1-X_B \),

but here Temperature \( \Rightarrow \) defects

form \( \Rightarrow \) some \( B \) are \( A \) & vice versa

\( \Rightarrow \) \( X_B \rightarrow X_B + \Delta x \) \( X_A \rightarrow X_A - \Delta x \)

\( \Rightarrow \) \( \Delta x \) defects an energy required to form (with Arrhenius)

\( \Rightarrow \) \( S(\Delta t) = -k [ \log(X_B + \Delta t) \log(X_B + \Delta t) \]

\( + (X_A - \Delta t) \log(X_A - \Delta t) ] \)

same way I have

\( X_B \rightarrow X_B - \Delta t \) \( X_A \rightarrow X_A + \Delta t \)

\( \Rightarrow S(\Delta t) \) \( \Delta t \) depends on energy to form defect with Arrhenius
Temperature = \( \text{Entropy} \) = Function of defects or off-stoichiometry phases.

FIGURE 7.3-6 Four binary isomorphous systems, Cu-Ni, Ge-Si, Ag-Au, and NiO-MgO.

PE 17

Solid solution at low temperature (not NICKEL-OXIDE + MAGNESIUM OXIDE.)
**Deviation from Ideality**

- **Ideal**
  \[ E_{AB} = \frac{1}{2} (E_{AA} + E_{BB}) \]

- **Custering Tendency**
  \[ E_{AB} > \frac{1}{2} (E_{AA} + E_{BB}) \Rightarrow E_{AB} \text{ is not "welcome" higher than ideal} \]

  It means that A prefers A to B
  B prefers B to A!

  \[ \min \# \text{ of A-B bonds in the solid phase} \]

  \[ \Rightarrow \text{to minimize total energy} \]

  Temperature tries to destroy as soon as possible the solid phase

  \[ \Rightarrow \min (E) \]

- **Ordering Tendency**
  \[ E_{AB} < \frac{1}{2} (E_{AA} + E_{AB}) \Rightarrow E_{AB} \text{ is "welcome" lower than ideal} \]

  It means that A prefers B to A
  B prefers A to B!

  \[ \max \# \text{ of A-B bonds} \]

  They want to order and resist to temperature (disorder) as much as possible!

  \[ \Rightarrow \text{Temperature needs to work hard to destroy ordering!} \]
NOW

IDEAL

\[ \text{min } F \Rightarrow \text{min } G \] (Entropy)

CLUSTERING TENDENCE

\[ E_{AB} > E_{AA} + E_{BB} \]

\[ \text{min } (\theta) \Rightarrow \text{min } 2 \]

CAN BE A "BANANA"

SOLID + LIQUID

? NO

because here

I would split

therefore

the lower part

would be just SOLID

"BANANA" LENS DOES NOT EXIST!!
CONGRUENT MELTING

SAME FOR ORDERING

$\Rightarrow$ NOT PHYSICAL

the LIQUIDUS & SOLIDUS

must "touch" at the min AND max

FIGURE 7.3-7  Progressive change in the form of the isomorphous phase diagram as the solid and liquid phases deviate from ideal behavior.
At its CONGRUENT MELTING POINT, the alloy solidifies/melts at a given temperature ($T_m(c)$) and concentration ($c$) and not in a temperature interval.

**Figure 7.3-8**
A binary phase diagram showing a congruently melting alloy of composition $X_{max}$. Two additional alloy compositions are shown.

If you want to make an alloy which resists at higher temperature than the constituents, than you need something like this.

If you want to make an alloy which melts at lower temperature than the constituents, than you need something like this.

PE21
EUTECTIC PHASE DIAGRAM

CLUSTERING (A like A better than B)
flow at low Temperature the two elements do not mix well solid solution disappears

\[ T = \text{solid solution above } T_{c} \text{ (critical)} \]

\[ T_{1} = \text{solid solution } A - \text{Rich} \]

\[ T_{2} = \text{solid solution } B - \text{Rich} \]

\[ \Delta_{A} = A, \quad \Delta_{B} = B \]

depending on the

Above \( T_{c} \)
COMPLETE SOLUBILITY

UNDER \( T_{c} \)
PARTIAL SOLUBILITY
A with B with sol & B with A with sol AmB

PE 22

FIGURE 7.4-1 The development of a eutectic reaction by increasing the clustering tendency in the solid phase:
(a) the diagram for an ideal system, and (b-d) increasing clustering tendency in the solid phase.
A binary eutectic phase diagram and the associated terms used to describe regions of a eutectic system.

**SOLVUS**

Solvus = max solubility of a specie in the other.

**EUTECTIC POINT**

Coexistence of 3 phases

\[ F = C - P + 2 \]

\[ \frac{2 - 3 + 1}{3} = 0 \]

**IN Variant < Eutectic point**

**FIGURE 7.4-7**

Representative microstructures of Al-Si alloys.

(a) The white areas are primary Al dendrites, and the dark areas are the eutectic constituent comprised of Al + Si. (b) Only the eutectic constituent is seen.

(c) Primary Si is seen as blocky particles. The dark needles and light areas are the eutectic constituent.

(Courtesy of Ralph Napoli.)

PE23
Melting Of An Eutectic Alloy

Go down at $X_E$ concentration through the Tm point.

Figure 7.4-3: A binary eutectic equilibrium phase diagram showing the changes in composition of the phases present as the temperature is changed by an amount $\Delta T$ above and below the eutectic isotherm.

With (E) $L \leftrightarrow \alpha + \beta$

At eutectic point we get $\Delta T \uparrow$ all liquid! 
$\Delta T \downarrow$ all solid!

Eutectic $X = X_E$

$X_E \rightarrow X_0 \rightarrow \beta + \beta$

Equilibrium solidification of an off-eutectic alloy of composition $X_0$.
SOLIDIFICATION OF AN EUTECTIC ALLOY

BUT OFF-EUTECTIC COMPOSITION

FIGURE 7.4-4 Equilibrium solidification of an off-eutectic alloy of composition $X_0$.

$T_1$

$\xrightarrow{\text{L}(X_{L1}) \leftrightarrow \text{L}(X_{S1}) + \text{L}(X_{L1})}$

$\xrightarrow{f_{S1}} \xrightarrow{f_{L1}}$

$f_{S1} = \frac{X_{S1} - X_0}{X_{L1} - X_{S1}}$ and $f_{L1} = \frac{X_0 - X_{S1}}{X_{L1} - X_{S1}}$

$T_2$

$\xrightarrow{\text{L}(X_{S2}) + \text{L}(X_{L2}) \xrightarrow{f_{S2}} \xrightarrow{f_{L2}}}$

$f_{S2} = \frac{X_{L2} - X_0}{X_{L2} - X_{S2}}$ and $f_{L2} = \frac{X_0 - X_{S2}}{X_{L2} - X_{S2}}$

$T_M = T_E \Rightarrow \xrightarrow{\text{L} \Rightarrow S(\beta) \Rightarrow \text{L}}$

$3$ PHASES

$X_{SE}$ NORM $X_{LE}$

$T_M = T_E \Rightarrow \xrightarrow{\text{L} \Rightarrow S(\beta) \Rightarrow \text{L}}$

$X_{SE}$ NORM $X_{LE}$

But a lot of

$\xrightarrow{\text{L} \Rightarrow S(\beta) \Rightarrow \text{L}}$

(A IF IT HAS $\text{S(\beta)}$ TO REARRANGE)

in the

$X_{SE}$ NORM $X_{LE}$

same way

fractions:

$f_{S} = \frac{X_{SE} - X_0}{X_{LE} - X_{SE}}$

$f_{S\beta} = \frac{X_0 - X_{SE}}{X_{SE} - X_{SE}}$

PE 25
At eutectic point, a lot of $\gamma$ and $\beta$ form simultaneously, and their morphology is different from the primary $\gamma$ and $\beta$. (It's because of the speed of the process. It's called eutectic ($\gamma + \beta$).)

Therefore below eutectic point, the alloy is a mixture of $\gamma +$ eutectic ($\gamma + \beta$).

Note that for any alloy with composition in the range $X_{SE} < X_0 < X_{SE}'$, at the eutectic temperature liquid of composition $X_{L,E}$ will transform to $\alpha$ and $\beta$ of compositions $X_{SE}$ and $X_{SE}'$, and that the relative amounts of $\alpha$ and $\beta$ formed from this liquid will be constant. In fact, this is what makes the eutectic reaction invariant.

**Example**

Composition 0.27 B. Calculate the following quantities:

a. The fraction of primary solid that forms under equilibrium cooling at the eutectic temperature.

b. The fraction of liquid with the eutectic composition that will transform to two solid phases below the eutectic isotherm.

c. The amount of $\alpha$ and $\beta$ that will form from the liquid just below the eutectic isotherm.

d. The total amount of $\alpha$ phase in the alloy at a temperature just below the eutectic temperature.

\[ f_{\alpha} = \frac{X_{L} - X_0}{X_{L} - X_{\alpha}} = \frac{37 - 27}{37 - 20} = 0.588 \]

This is $\alpha$-primary. For $X_{SE} = 20\%$.

---

\( \text{PE} 26 \)
b. The fraction of liquid with the eutectic composition that will transform to two solid phases below the eutectic isotherm.

\[ f_{\text{L}}^{\text{Eut}} = \frac{X_{\alpha} - X_{\Lambda}}{X_{\Lambda} - X_{\alpha}} = \frac{27 - 20}{37 - 20} = 0.412 \]

\[ X_{\text{LE}} = 37\% \]

\[ = 1 - f_{\text{P}} \]  
\[ P_{\text{E27}} \]

\[ L_{\text{Eut}} \text{ loss} \]

\[ c. \text{ The amount of } \alpha \text{ and } \beta \text{ that will form from the liquid just below the eutectic isotherm.} \]

\[ X_{\text{BE}} = 37\% \]  
\[ (\text{Eut, liquid just below the eutectic point}) \]

\[ \text{it becomes solid at eut. solid } \alpha + \beta \text{ with } f_{\beta} \]  
\[ \begin{align*} f_{\alpha} &= \frac{X_{\beta} - X_{\alpha}}{X_{\beta} - X_{\alpha}} = \frac{73 - 37}{73 - 20} = 0.679 \\ f_{\beta} &= \frac{X_{\text{L}} - X_{\beta}}{X_{\beta} - X_{\alpha}} = \frac{37 - 20}{73 - 20} = 0.321 \end{align*} \]

\[ \Rightarrow \text{ so have } \frac{\beta}{\alpha} + \text{Eut} (\beta + \alpha) \]

\[ f_{\alpha} = 0.588 \]

\[ f_{\beta} = 0.321 \]

\[ f_{\text{L}} + f_{\text{S}} = 0.412 \]

\[ \begin{align*} f_{\text{P}} + f_{\text{Eut}} + f_{\text{Tot}} &= f_{\alpha} + f_{\beta} \\ 0.588 + f_{\text{Eut}} &= 0.412 + 0.679 = 0.280 \end{align*} \]

\[ f_{\text{Eut}} = 0.412 \times 0.321 = 0.132 \]
d) The total amount of $\alpha$ phase in the alloy at a temperature just below the eutectic temperature.

$$f^\text{tot}_\alpha = f^\text{P}_\alpha + f^\text{EUT}_\alpha$$

OR

$$\Delta = f^\text{EUT}_\alpha$$

OR

$$f^\text{tot}_\alpha = f^\text{P}_\alpha + f^\text{EUT}_\alpha = 0.588 + 0.280 = 0.868$$

Alternatively, since the microstructure is composed of just two phases, $\alpha + \beta$, the total fraction of $\alpha$ must be given by:

$$f^\text{tot}_\alpha = 1 - f^\text{EUT}_\beta = 1 - 0.132 = 0.868$$
FIGURE 7.4-6

ALUMINUM- SI LCN (CHIPS)

CARS
(PISTONS)
(HARD, Si =>
WEAR
RESISTANCE)

Look at
Page PE23

(AGING)
(TENDENCY)

AL = LIGHT

PE 29
FIGURE 7.4-7
Representative microstructures of Al-Si alloys.
(a) The white areas are primary Al dendrites, and the dark areas are the eutectic constituent comprised of Al + Si. (b) Only the eutectic constituent is seen. (c) Primary Si is seen as blocky particles. The dark needles and light areas are the eutectic constituent. (Courtesy of Ralph Napolitano)

Properties vs Concentration
PE 30
HOW TO MEASURE

melt & watch T(t) behaviour

Temperature profiles (c)

Properties profile (c)

PE31
TWO EUTECTICS

A likes A more than B \( \Rightarrow \) \( E_{AB} > \frac{1}{2} (E_{AA} + E_{AB}) \) \( \Rightarrow \) CLUSTERING TEM

\[ \Rightarrow \text{WEAKER SOUL SOLUTION} \]

\[ \Rightarrow \text{STRONGER LIQUID} \]

\[ T \]

A likes B more than A \( \Rightarrow \) \( E_{AB} < \frac{1}{2} (E_{AA} + E_{AB}) \) \( \Rightarrow \) ORDERING TEM

\[ \Rightarrow \text{STRONGER SOLID SOLUTION} \]

\[ \Rightarrow \text{WEAKER LIQUID} \]

\[ T \]

TAKE 2 ATOMS (AA), (AB), (BB)

If (AA) likes (AA) more than (AB) (depends from structure)

\( \Rightarrow \) \( E_{AA-AB} > \frac{1}{2} (E_{AA-AA} + E_{AA-BB}) \)

\[ \Rightarrow \]

\[ T \]

STOPS AT 80% ONE OR ELSEWHERE

IF low temperature IMMISCIBILITY of AA & AB

(NO SOLID SOLUTION) \( \Rightarrow \)
the system can form an eutectic between 0 & 50%.

Rule: between two chemical compounds you can form an eutectic (can = may ≠ must = has to).

**Figure 7.4-11** (a) A binary equilibrium phase diagram containing two eutectic reactions illustrating solid solution ranges, an intermediate phase B, and a congruent melting reaction. (b) When the solubility of the intermediate phase becomes limited, the line compound AB results.
Examples

Reactions at the invariant points (ab)

1. Eutectic reaction at $T_{E_1}$ and $X_{E_1}$; $L \rightleftharpoons \alpha + \beta$
2. Eutectic reaction at $T_{E_2}$ and $X_{E_2}$; $L \rightleftharpoons \beta + \gamma$
3. Congruent melting at $T_c$ and $X_c$; $L \rightleftharpoons \beta$

---

If no solubilities

A host mixing with B
But only in the liquid
Please they do / because the higher entropy of
The liquid

PE34
PERITECTIC SYSTEMS

1) When A alloys with B (CLUSTERING) at low temperature (MISCIBILITY GAP)

2) Melting point very different

3) A alloys with B else at high temper.
   (CLUSTERING OF LIQUIDS) = LENS BECOME WIDER

LITTLE LIQU. CLUST

A LOT OF LIQ. CLUSTER

SOLID SOLUTION MISCIBILITY GAP

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FIGURE 7.5-1 Development of a peritectic system by increasing the clustering tendencies of the solid and liquid phases. The clustering tendency for the solid is greater than that of the liquid. (Source: Adapted from Albert Prince)
FIGURE 7.5-2 (a) A binary peritectic phase diagram and the associated terms used to describe regions of a peritectic system. (b) A simple peritectic system showing the equilibrium cooling of an alloy whose composition is the peritectic composition $X_p$, and (c) the corresponding cooling curve for alloy $X_p$.

**TABLE 7.5-1**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Above peritectic</th>
<th>Below peritectic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T = T_P + E$</td>
<td>$T = T_P - E$</td>
</tr>
<tr>
<td>$X_1$</td>
<td>$0.125 - 0.09$</td>
<td>0</td>
</tr>
<tr>
<td>$X_2$</td>
<td>$0.53 - 0.09$</td>
<td>$0.17 - 0.125$</td>
</tr>
<tr>
<td>$X_3$</td>
<td>$0.53 - 0.09$</td>
<td>$0.563$</td>
</tr>
<tr>
<td></td>
<td>$0.53 - 0.09$</td>
<td>$0.437$</td>
</tr>
<tr>
<td></td>
<td>$X_{C_{Fe}} = 12$</td>
<td>$X_{C_{Fe}} = 17$</td>
</tr>
</tbody>
</table>

**FIGURE 7.5-3** A simple peritectic diagram showing three specific alloy compositions. Refer to Example 7.5-1 for a discussion of this phase diagram.
**MONOTECTIC PHASE DIAGRAM**

- The eutectic but for liquids:
  - Liquid A + Liquid B ⇒ Solid at
  - Miscibility gap for eutectic (region L₁ + L₂)
  - Solid Liquid 1 & Liquid 2 outside

**OIL + WATER**

- Mix only at high temp

**Figure 7.6-1** The limiting case of the monotectic reaction occurs when there is effectively no mutual solubility in either the liquid or solid phase.

**PE 37**

- Summary:
  - Eutectic: \( L₁ + L₂ \Rightarrow L₃ \)
  - Peritectic: \( L₁ + L₂ \Rightarrow L₄ \)
  - Monotectic: \( L₁ \Rightarrow L₂ \)
  - C + W: only very fine
  - Mixture + second invariant
  - Mass \( F = C - P + \frac{Q}{2} \)
  - Odd point

**3 phase**
1) For students: Everything is complex.
2) For professors: Complex systems = many phase regions & invariant points.

Remember:

- **CONGRUENT MELTING**
- **EUTECTIC POINT**
- **PERITECTIC POINT**
- **NONEUTECTIC POINT**

**FIGURE 7.7-1** (a) Complex phase diagram containing a peritectic and two eutectic reactions, and (b) the invariant reactions in (a) emphasized along with their symbolic representations. When the $\beta$ phase is heated to the peritectic temperature, an incongruent melting reaction occurs at $T_p$, the peritectic temperature.
IDEA: BREAK PHASE DIAGRAMS IN AS MANY PART AS "POSSIBLE" \( \implies \) IT BECOMES EASIER

EXTRA TROUBLE:

\( \text{INCONGRUENT MELTING:} \)

\[ L + ? \rightarrow \beta \]

\( \text{If liquid solidifies to a phase with different concentration?} \)

\( L + ? \rightarrow \beta \)

\( \checkmark \text{ something else } \)

\( X_{\beta} \neq X_{L} \)

\( L + \gamma \rightarrow \beta \text{ in peritectic} \)

IF NO SOLUBILITIES ON INTRA-HOLOPHASE

PHASES (BROAD CONCENTRATION) \( \rightarrow \) COMPOUNDS

\( \gamma, \beta, \delta \text{ } \rightarrow \text{ } A, B, A_{2}B \text{...} \)

**Figure 7.7-2** A diagram similar to Figure 7.7-1, but the \( \beta \) and \( \gamma \) are seen as line compounds. The \( \alpha \) and \( \delta \) phases are terminal solid solutions with essentially no solubility. Thus, they are simply labeled A and B, corresponding to the pure components.
It is worth noting that $\alpha$(Ni-Al) is often called $\gamma'$ and is the basis of strengthening in Ni-base superalloys.

\[ X' \text{ = Fundamental in strengthening of Ni-Superalloys} \]

(Prepituates of $\gamma'$ form as agglomerates that stop dislocation movements, break plasticity, no deformation, keep elasticity permanent)

Superalloy!!
PHASE EQUILIBRIA WITH SOL-SOL REACTION

LIQUID REACTION
L → γ + β EUTECTIC
L + γ → β PERITECTIC
L + γ → L₂ + Q NONOTECTIC

SUBSTITUTE
L with a phase solid
γ + Q → γ + β PERITECTIC
γ + γ → γ + β NONOTECTIC

FIGURE 7.8-1
A general eutectoid equilibrium phase diagram with associated phase definitions.

EUTECTOID SYSTEM
SOLID PHASE DECOMPOSES INTO 2 SOLID PHASES
γ → γ + β

EUTECTIC

EUTECTOID

REACTION is fast because diffusion in L
γ fast → γ, β slow to form 8 separate

 reaction is slow diffusion in solid along boundary
IRON-CARBON HAS EUTECTOID

See: NO SOLUBILITY OF Fe in Fe₃C

FIGURE 7.8-2 The Fe-Fe₃C system with the important phase fields defined.

BOOK: TAKE δ (austenite) with 0.77% w C & cool down

EUTECTOID @ 727°C

δ ↔ 3 + (γ + Fe₃C)

AUSTENITE

FERRETI

PEARLITE

[See: solubility of C in δ (Fcc-Fe) is bigger than in γ (Bcc-Fe)]

WHY?

As long as you have δ (with > 0.022% w C → you get pearlite)

IN PRACTICAL WORDS:

WE HAVE PEARLITE ALL OVER THE PLACE